Effects of Reaction Conditions on Gasification of Coal–Residual Oil Slurry

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Introduction

In the face of energy crisis and environmental pollution, the technology for coal gasification is being developed as a part of "Sunshine Project" promoted by the Ministry of International Trade and Industry (MITI). Petroleum, however, will hold by far the largest share in Japan's primary energy supply for the next decades. While the utilization of heavy oil such as vacuum residue is limited from a point of view of the air pollution because of difficult desulfurization.

Therefore, in 1974 we have started the development of "Hybrid Gasification Process" in which coal and residual oil are simultaneously gasified to clean fuel gas. This report briefly describes the process and experimental results.

Process Description

A flow diagram of Hybrid Gasification Process is shown in Figure 1. Pulverized coal is mixed and stirred with residual oil to form a slurry, which is pumped to the pressurized fluidized bed gasifier with atomizing steam. The slurry is converted into gas and char by thermal cracking reactions in the upper zone of the fluidized bed. The char produced is further gasified with steam and oxygen.

The gas leaving the gasifier is scrubbed in oil and then in water quench to remove tar, dust and steam. A conventional gas clean up system is used to absorb carbon dioxide and hydrogen sulfide from the gas. If SNG is required, the product gas is shifted and methanated.

The advantages of the process are
(1) Almost all grades of coal and residual oil can be simultaneously converted to clean fuel gas.
(2) Raw materials are transported and fed to the pressurized gasifier without difficulty by means of slurry.
(3) The gasifier consists of a single fluidized bed and the gasification reactions proceed in two stages —— slurry thermal cracking and char partial oxidation. This simple structure of the gasifier achieves easy control and high thermal efficiency.

Experimental

In order to investigate the gasification characteristics and to improve the process, experiments were conducted in the pressurized gasification apparatus shown in Figure 2. The gasifier has the inner diameter of 120mm in the upper zone and 80mm in the lower zone. The height of each zone is 2000mm. The temperatures in the gasifier are controlled by the surrounding electric heaters.

At the beginning of each experiment, pulverized and sieved coal in the coal hopper is charged and fluidized with steam and oxygen. Then the $200^{\circ}C$ pre-heated slurry with atomizing steam is fed to the middle part of the fluidized bed. The bed height above the slurry feeding point is 700mm. After dust, tar and steam in the product gas are removed in cyclones, scrubber and quencher, the gas pressure is reduced and its composition and its flow rate are measured.

Since a part of the gas is produced by the heat supplied from the external heaters, the gas yeilds of these experiments are somewhat different from the ones produced in the purely internally fired gasifier. Therefore, we have examined the characteristics of thermal cracking and partial oxidation separately. The gas produced in the thermal cracking zone is considered as follows.

$$G_S = G_T - G_C \qquad\qquad 1)$$

where G_S : gas production rate in the slurry thermal cracking zone,
          G_C : gas production rate in the char partial oxidation zone,
          G_T : total gas production rate in the gasifier when slurry thermal cracking
               and char partial oxidation occur simultaneously.
G_C can be measured when slurry feeding is stopped and only the char partial
oxidation reaction takes place.

Feeding materials are shown in Table I. Taiheiyo coal, mined in Hokkaido, was chosen for this study because it is the most practicable for gasification use in domestic coals.

Table I. Raw materials

Taiheiyo coal		Gach Saran Vacuum Residue	
Proximate analysis (wt%)		Boiling point ($^\circ$C)	>550
Moisture	5.3	Asphaltene (wt%)	10.4
Ash	14.4	Conradson carbon (wt%)	21.8
Fixed carbon	37.7	Metal content (ppm) V	318
Volatile matter	42.5	Ni	112
Ultimate analysis (wt%, daf)		Ultimate analysis (wt%)	
C	76.6	C	85.0
H	6.5	H	10.8
N	1.0	N	0.1
O	15.3	O	–
S	0.6	S	3.5
Heating value (kcal/kg) 6580		Heating value (kcal/kg)	10090

(Note) Feed slurry ; Coal/Residual oil : 30/70 (wt. ratio)
                 Coal size : 40–140 mesh (0.105–0.42 mm)
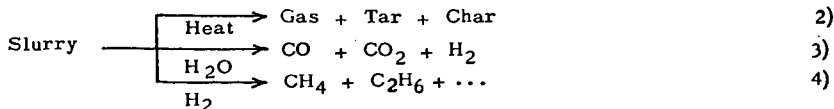   Initially charged coal size : 25–40 mesh (0.42–0.71 mm)

Gasifier temperatures were controlled by oxygen feed rate and the surrounding electric heaters between 800 and 950°C in the lower partial oxidation zone and between 700 and 800°C in the upper thermal cracking zone. Reaction pressures were varied from 5 to 20 atm.

Results and Discussion

(1) Characteristics of Slurry Thermal Cracking Reaction.

Figure 3 shows the effects of temperature and pressure on the product yield of slurry thermal cracking. The main components produced are hydrogen, methane, carbon monoxide and carbon dioxide. The yields of these gases increase with temperature (T_S) and pressure, while yield of by-product tar decreases as pressure rises.

In this zone, following reactions take place.

$$\text{Slurry} \xrightarrow{\begin{array}{c}\text{Heat}\\ H_2O\\ H_2\end{array}} \begin{cases} \text{Gas} + \text{Tar} + \text{Char} & 2) \\ CO + CO_2 + H_2 & 3) \\ CH_4 + C_2H_6 + \cdots & 4) \end{cases}$$

Overall heat of reaction ΔH_R can be estimated by the next equation.

$$\Delta H_R = \sum_R N\,\Delta H_C - \sum_P N\,\Delta H_C \qquad\qquad 5)$$

where the first term on the right side refers to the summation of heats of combustion for the reactants and the second term for the products.
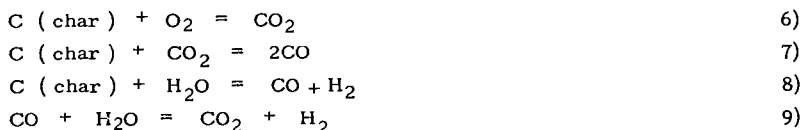
The overall heat of reaction estimated by the measured heats of combustion for

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slurry, tar and char are shown in the upper columns of Figure 3. As shown in the fugure, ΔH_R increases with increasing temperatures and decreases with increasing pressures.

The characteristics stated above definitely show that endothermic reactions such as thermal cracking and steam reforming are dominant at higher temperatures and exothermic hydrogasification takes place at higher pressures.

(2) Characteristics of Char Partial Oxidation Reaction.

The main components in the gas produced in the partial oxidation zone are hydrogen, carbon monoxide and carbon dioxide. Therefore, the main reactions are supposedly as follows.

$$C \text{ (char) } + O_2 = CO_2 \qquad\qquad 6)$$

$$C \text{ (char) } + CO_2 = 2CO \qquad\qquad 7)$$

$$C \text{ (char) } + H_2O = CO + H_2 \qquad\qquad 8)$$

$$CO + H_2O = CO_2 + H_2 \qquad\qquad 9)$$

The approach of these reactions toward equilibrium is indicated in Figure 4. Kp and Kp' are the equilibrium constant and the observed partial pressure ratio respectively. It is apparent from Figure 4 that the carbon – carbon dioxide reaction and the carbon–steam reaction are far from equilibrium for all of the run conditions tested, while the observed ratios for the shift reaction approach the equilibrium constant at pressures above 10 atm. in the range of 800 to 950°C.

(3) Heat and Material Balance in Gasifier.

Based on the results described above, the heat and material balance in the gasifier without external heating was investigated. As shown in Figure 5, following assumptions are made.

 (i) Q_S, the heat required in the slurry thermal cracking zone, is represented by Equation A, where ΔH is the heat required to warm the reactants from the inlet temperature to the reaction temperature T_S.

 (ii) In the char partial oxidation zone, Reaction 6 – 9 take place, Reaction 9 being in equilibrium. Overall heat of reaction in this zone raises the temperature of fluidizing char and gas, and this heat is released in the thermal cracking zone. Therefore, in the steady state, heat balance in the gasifier can be represented by Equation B, where Q_{RC} and Q_{GC} represent the quantities of heat transferred by char and gas, respectively.

(iii) In the steady state, the amount of char produced in the thermal cracking zone is equal to the amount of char gasified in the partial oxidation zone.

The conclusions from this investigation are summarized in Figure 6. It is indicated in Figure 6-a that the thermal efficiency, i.e., the ratio of the heating value of product gas to that of raw materials, has the maximum value at about 750°C. This is because the heat required in the thermal cracking zone is so large at higher temperatures that the amount of carbon dioxide increases. When pressures increase at constant temperature, as shown in Figure 6-b, both the product gas heating value and the thermal efficiency increase and oxygen feed rate decreases. This is because hydrogasification reactions play a more important role at higher pressures.

The typical heat and material balance is shown in Figure 7. The heating value of the raw gas is 4070 kcal/Nm³(460 Btu/scf), and 5970 kcal/Nm³(670 Btu/scf) after removal of carbon dioxide and hydrogen sulfide on the basis of dry gas. The thermal efficiency is about 75%.

The by-product tar yield is rather high (13–15 wt%) in this process. The tar can be either recycled to the gasifier or utilized as fuel oil, binder, raw materials for chemical industries and so on.

In addition to the study mentioned above, recently a low pressure (max. 3 atm) internally fired gasifier with a 300mm diameter has been operated to solve the possible mechanical and operational problems.

On the basis of these researches, a 12 t/D pilot plant is being designed, and it will be constructed in 1980.

Acknowledgement

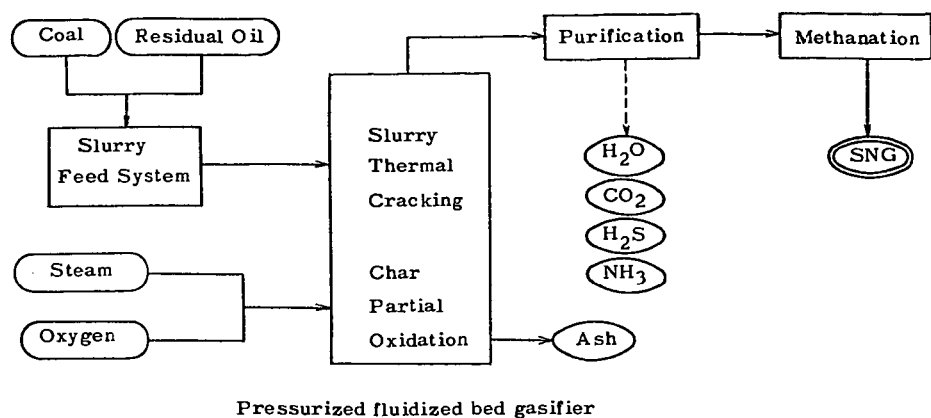Pressurized fluidized bed gasifier

Figure 1. Coal-Residual Oil Hybrid Gasification Process
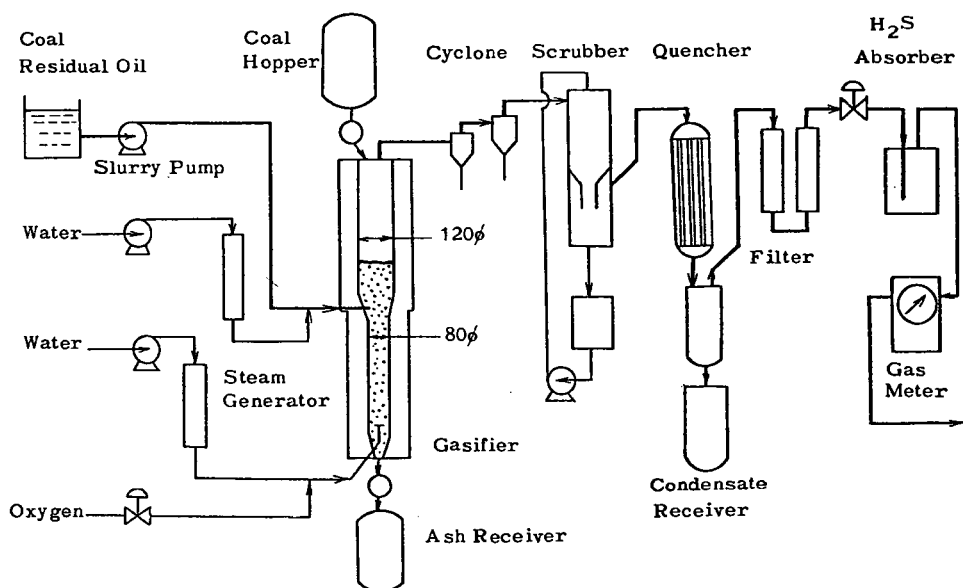

Figure 2. Pressurized fluidized bed gasification apparatus
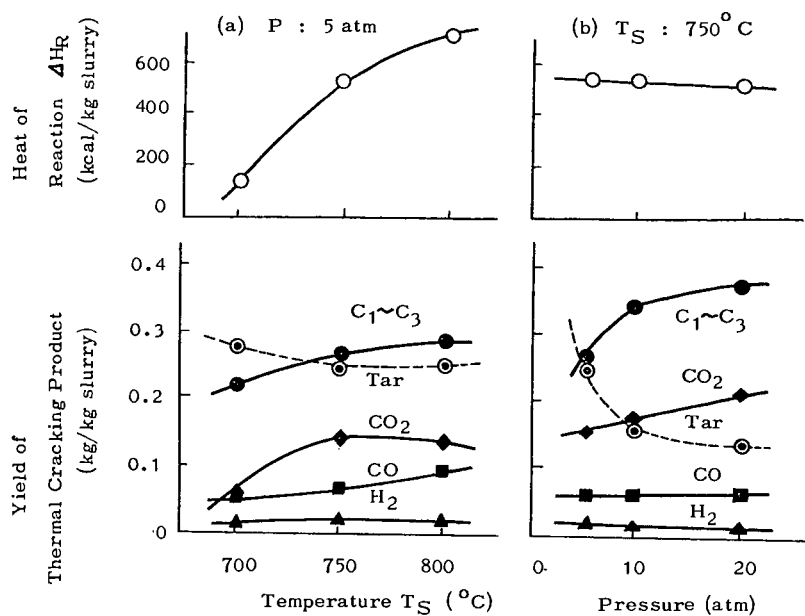
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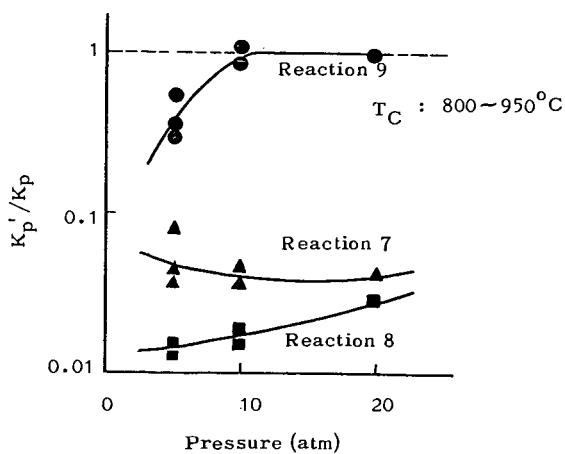Figure 3. Effects of temperature and pressure on slurry thermal cracking

Figure 4. Comparison of observed partial pressure ratio of partial oxidation gas with equilibrium constant

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Product Gas

Slurry (200 °C)	Thermal Cracking T_S °C
Steam (300 °C)	

Char | Fluidizing Char (Q_{RC}) | Gas (Q_{GC})

Steam (300 °C)	Partial Oxidation T_C °C
Oxygen (25 °C)	

Ash

ΔH_R

Slurry $\xrightarrow[\text{H}_2]{\text{Heat} \ \text{H}_2\text{O}}$

$$\text{Gas} + \text{Tar} + \text{Char} \qquad 2)$$
$$\text{CO} + \text{CO}_2 + \text{H}_2 \qquad 3)$$
$$\text{CH}_4 + \text{C}_2\text{H}_6 + \ldots \qquad 4)$$

$$Q_S = \Delta H_R + \Delta H \qquad A)$$

$$Q_S = Q_{RC} + Q_{GC} \qquad B)$$

$$C + O_2 \longrightarrow CO_2 \qquad 6)$$
$$C + CO_2 \longrightarrow 2CO \qquad 7)$$
$$C + H_2O \longrightarrow CO + H_2 \qquad 8)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad 9)$$
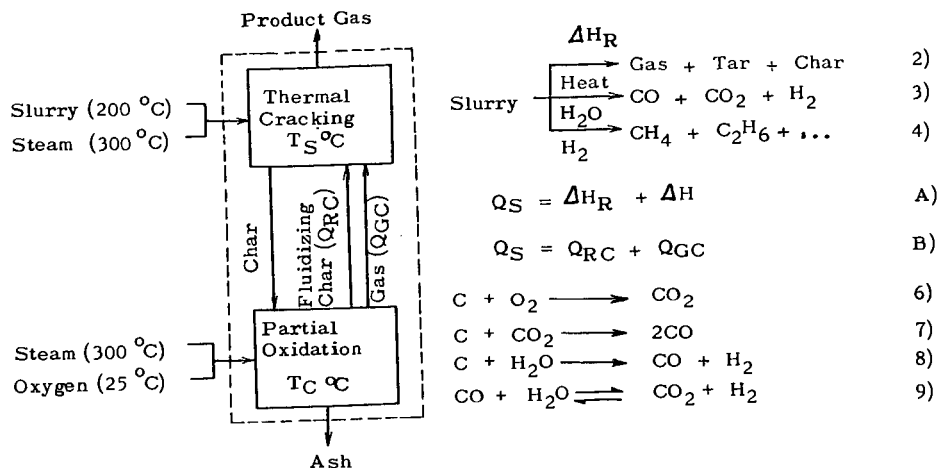
Figure 5. Reaction model in Hybrid Gasifier

Steam Feed Rate : 1.6 kg/kg slurry

(a) P : 5 atm   (b) T_S : 750 °C

Thermal Efficiency (%)

Gas Heating Value (kcal/Nm^3)

Oxygen Feed Rate (kg/kg slurry)

Temperature T_S (°C)   Pressure (atm)
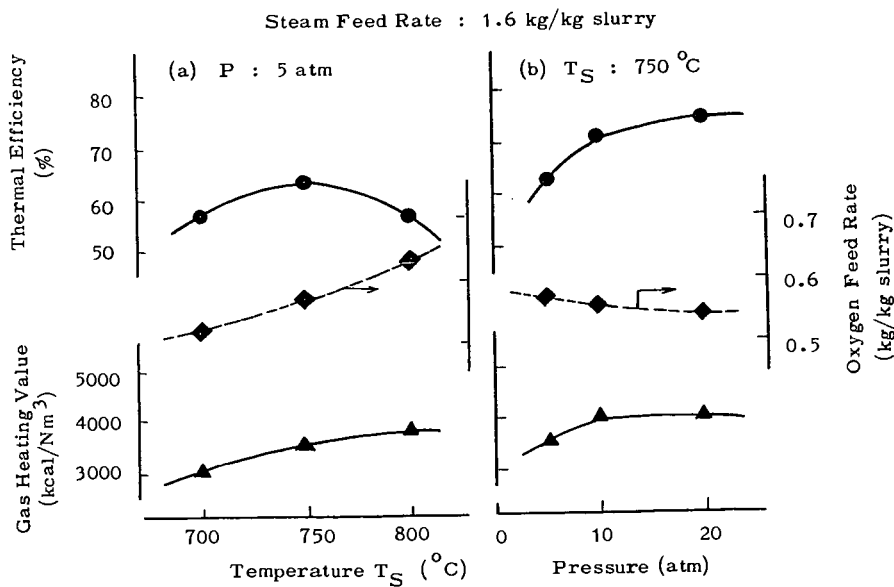
Figure 6. Effects of temperature and pressure on Hybrid Gasification Process

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Material Balance

Feed			Product Gas	Raw Gas ◇1	Purified Gas ◇2
Slurry	1.0 kg				
Steam	1.6 + 0.4 kg				
Oxygen	0.54 kg				
Composition (vol%, dry)			H_2	33.0	49.5
			CO	10.1	15.1
			CO_2	32.1	-
			CH_4	17.6	26.4
			C_2's	5.5	8.1
			C_3's	0.6	0.9
			H_2S	1.1	-
Gas Heating Value (kcal/Nm^3) [Btu/scf]				4072 [457]	5974 [670]
Gas Volume (Nm^3/kg slurry)				1.698	1.135

Heat Balance

100 → Pre-treatment → Gasification → Quenching → Purification

Heat Loss 0.2
Ash 0.6
Dust 1.6
Tar 13.4
H_2S 1.2
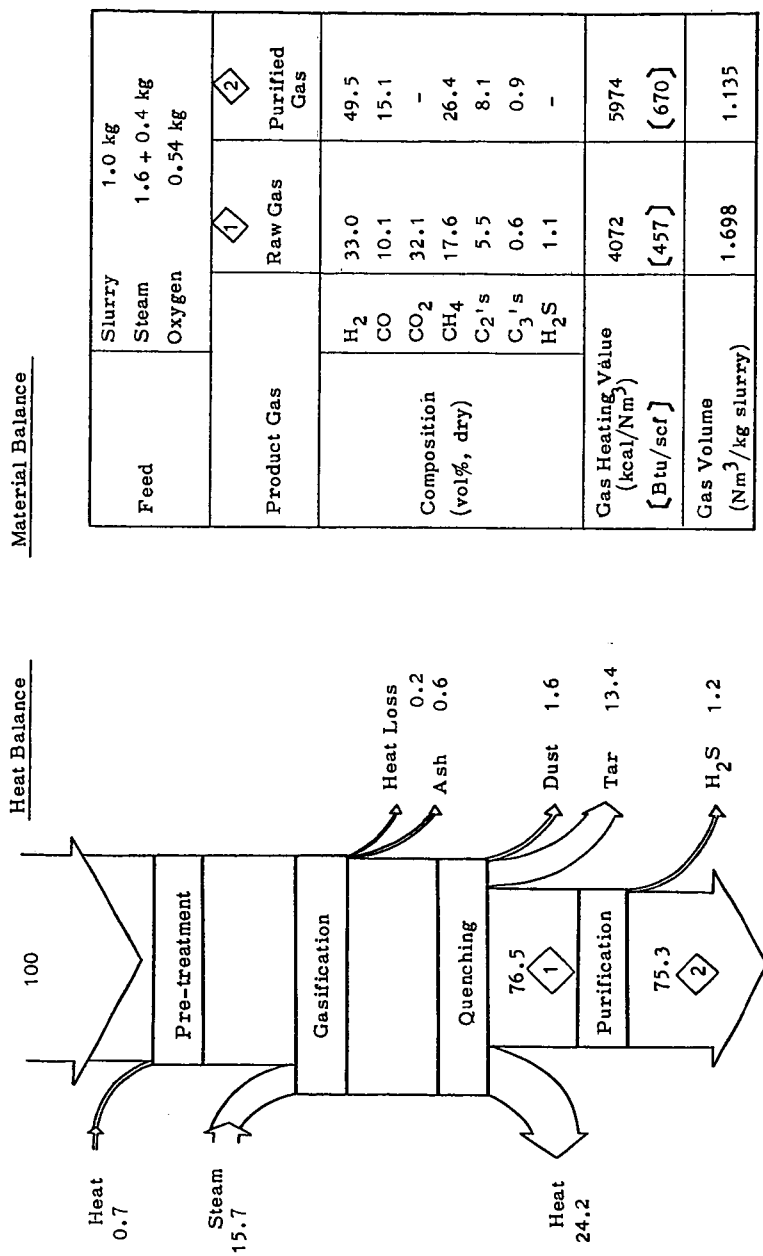
Heat 0.7
Steam 15.7
Heat 24.2

76.5 ◇1
75.3 ◇2

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Figure 7. Heat and material balance in Hybrid Gasification Process